

What is claimed is:

1. A method of free radical polymerization comprising (1) forming a mixture of one or more monomers, at least one free radical source and a chain transfer agent, wherein the chain transfer agent comprises a thio group; (2) subjecting the mixture to polymerization conditions, wherein a resulting polymer comprises thio groups; (3) contacting the resulting polymer with a free radical source and a monomer having a propagation rate constant ( $k_p$ ) less than 2000 under cleavage reaction conditions; and (4) activating the free radical source to generate radicals, wherein at least 50% of the thio groups are replaced with a group of interest other than hydrogen.

2. The method of claim 1, wherein the monomer contacting the resulting polymer has a  $k_p$  of less than 1000.

3. The method of claim 1, wherein the monomer with little to no homopolymerizability has a  $k_p$  of less than 500.

4. The method of claim 1, wherein the monomer with little to no homopolymerizability has a  $k_p$  of less than 300.

5. The method of claim 1, wherein the free radical source is introduced continuously throughout the cleavage reaction.

6. The method of claim 1, wherein the monomer with a  $k_p$  less than 2000 is selected from the group consisting of maleimide, N-substituted maleimides, maleic anhydride, maleic acid, fumaric acid, maleic esters, fumaric esters, allyl and methallyl compounds, vinyl ethers, vinyl sulphonates, vinyl phosphonates, 1,3-butadiene derivatives, itaconic acid,  $\alpha$ -alkylstyrene,  $\alpha$ -ethylacrylate, cis and trans stilbene, and combinations thereof.

7. The method of claim 1, wherein the monomer with a  $k_p$  less than 2000 is selected from the group consisting of maleimide, N-phenylmaleimide, N-methylmaleimide, N-ethylmaleimide, N-benzylmaleimide, N-propylmaleimide, N-(4-ethylphenyl)maleimide, N-(4-acetylphenyl) maleimide, N-(para-tolyl)- maleimide, N-cyclohexyl maleimide N-dodecyl maleimide, N-tert-butyl maleimide, N-isopropyl maleimide, N-(2-hydroxyethyl) maleimide, N-(3-hydroxypropyl) maleimide, di-n-butyl maleate, di-n-amyl maleate, diethyl maleate, diisoamyl maleate, dimethyl maleate, diphenyl maleate, and di-n-propylmaleate, di-n-amyl fumarate, diethyl fumarate, diisoamyl fumarate, diisobutyl

fumarate, diisopropyl fumarate, dimethyl fumarate, diphenyl fumarate, di-n-propyl fumarate, (meth)allylsulfonate, (meth)allylglycidylether, (meth)alkylvinylether, (meth)allylbutyl ether, (meth)allylethyl ether, (meth)allylmethyl ether, and combinations thereof.

8. The method of claim 1, wherein the monomer with a  $k_p$  less than 2000 is selected from the group consisting of N-phenylmaleimide, N-methylmaleimide, N-ethylmaleimide, N-benzylmaleimide, N-propylmaleimide, and combinations thereof.

9. The method of claim 1, wherein at least one of the one or more monomers in the monomer mixture is an acrylate.

10. The method of claim 1, wherein all of the monomers in the monomer mixture are acrylates.

11. The method of claim 1, wherein cleavage reaction conditions comprise a molar ratio of between 0.5:1 and 10:1 for the monomer having a  $k_p$  less than 2000 to the thio groups in the polymers for which cleavage is desired.

12. The method of claim 1, wherein cleavage reaction conditions comprise a molar ratio of between 1.0:1 and 5:1 for the monomer having a  $k_p$  less than 2000 to the thio groups in the polymers for which cleavage is desired.

13. The method of claim 1, wherein cleavage reaction conditions comprise a molar ratio of between 1.5:1 to 3:1 for the monomer having a  $k_p$  less than 2000 to the thio groups in the polymers for which cleavage is desired.

14. A polymer formed by the method of claim 1.

15. The polymer of claim 14, wherein said polymer is a block copolymer.

16. The polymer of claim 14, wherein said polymer is a random copolymer.

17. The method of claim 1, wherein at least 85% of the thio groups are replaced with a moiety comprising the radicals generated in step (4).

18. The method of claim 1, wherein at least 95% of the thio groups are replaced with a moiety comprising the radicals generated in step (4).

19. A method of cleaving at least a portion of a thiocarbonylthio group from an end of a polymer, the method comprising forming a mixture of the polymer, at least one free radical source, and a monomer with propagation rate constant ( $k_p$ ) less than 2000, and subjecting the mixture to cleavage reaction conditions.

20. The method of claim 19, wherein the source of free radicals is selected from the group consisting of peroxides, hydroperoxides, peresters, peracids, percarbonates and azo compounds.

21. The method of claim 19, wherein an additional reagent is added which interacts in a redox reaction with the free radical source to liberate radicals..

22. The method of claim 19, wherein cleavage reaction conditions comprise a molar ratio of between 0.5:1 and 10:1 for the monomer having a  $k_p$  less than 2000 to the thio groups in the polymers for which cleavage is desired.

23. The method of claim 19, wherein cleavage reaction conditions comprise a molar ratio of between 1.0:1 and 5:1 for the monomer having a  $k_p$  less than 2000 to the thio groups in the polymers for which cleavage is desired.

24. The method of claim 19, wherein cleavage reaction conditions comprise a molar ratio of between 1.5:1 to 3:1 for the monomer having a  $k_p$  less than 2000 to the thio groups in the polymers for which cleavage is desired.

25. The method of claim 19, wherein the monomer has a  $k_p$  less than 1000.

26. The method of claim 19, wherein the monomer has a  $k_p$  less than 500.

27. The method of claim 19, wherein the monomer has a  $k_p$  less than 300.

28. The method of claim 19, wherein the monomer with a  $k_p$  less than 2000 is selected from the group consisting of maleimide, N-substituted maleimides, maleic anhydride, maleic acid, fumaric acid, maleic esters, fumaric esters, allyl and methallyl compounds, vinyl ethers, vinyl sulphonates, vinyl phosphonates, 1,3-butadiene derivatives, itaconic acid,  $\alpha$ -alkylstyrene,  $\alpha$ -ethylacrylate, cis and trans stilbene, and combinations thereof.

29. The method of claim 19, wherein the monomer with a  $k_p$  less than 2000 is selected from the group consisting of maleimide, N-phenylmaleimide, N-methylmaleimide, N-ethylmaleimide, N-benzylmaleimide, N-propylmaleimide, N-(4-ethylphenyl)maleimide, N-(4-acetylphenyl) maleimide, N-(para-tolyl)- maleimide, N-cyclohexyl maleimide N-dodecyl maleimide, N-tert-butyl maleimide, N-isopropyl maleimide, N-(2-hydroxyethyl) maleimide, N-(3-hydroxypropyl) maleimide, di-n-butyl maleate, di-n-amyl maleate, diethyl maleate, diisoamyl maleate, dimethyl maleate, diphenyl maleate, and di-n-propylmaleate, di-n-amyl fumarate, diethyl fumarate, diisoamyl fumarate, diisobutyl fumarate, diisopropyl fumarate, dimethyl fumarate, diphenyl fumarate, di-n-propyl fumarate, (meth)allylsulfonate, (meth)allylglycidylether, (meth)alkylvinylether, (meth)allylbutyl ether, (meth)allylethyl ether, (meth)allylmethyl ether, and combinations thereof.

30. The method of claim 19, wherein the monomer with a  $k_p$  less than 2000 is selected from the group consisting of N-phenylmaleimide, N-methylmaleimide, N-ethylmaleimide, N-benzylmaleimide, N-propylmaleimide, and combinations thereof.

31. The method of claim 19, wherein said polymer is a block copolymer.

32. The method of claim 19, wherein the polymer is a random copolymer.

33. The method of claim 19, wherein at least 85% of the thio groups are replaced with a moiety other than hydrogen.

34. The method of claim 19, wherein at least 95% of the thio groups are replaced with a moiety other than hydrogen.

35. The method of claim 19, wherein the free radical source is introduced continuously throughout the cleavage reaction.

36. A method of free radical polymerization comprising (1) forming a mixture of one or more acrylate monomers, at least one free radical source and a chain transfer agent, wherein the chain transfer agent comprises a thiocarbonylthio group; (2) subjecting the mixture to polymerization conditions, wherein a resulting polymer comprises thiocarbonylthio groups; and (3) contacting the resulting polymer with a free

radical source and a monomer having a propagation rate constant ( $k_p$ ) less than 2000 under cleavage reaction conditions.

37. The method of claim 36, wherein the monomer having a  $k_p$  less than 2000 is selected from the group consisting of N-phenylmaleimide, N-methylmaleimide, N-ethylmaleimide, N-benzylmaleimide, N-propylmaleimide, and combinations thereof.

38. The method of claim 36, wherein the free radical source is an initiator.